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ABSTRACTS FROM THE ORIGINAL PAPERS.

The Electrolysis of Nitrobenzol at the Mercury dropping cathode

Part I. The reduction potential of nitrobenzol.

By Masuzo Shikata.

The dropping mercury cathode has been found to give exact deposition potentials of metallic ions from their aqueous as well as alcoholic solutions.

It is naturally of interest to see how far this method can be applied for the study of cathodic reduction of organic substances.

Nitrobenzol has been chosen as one of the typical organic electrolytic reductions hitherto systematically studied.

Series of experiments have been carried out in acidic, neutral and alkaline solutions.

In acidic as well as neutral media the relation between reduction potential and system nitrobenzol–nitrosobenzol–hydrogenions follows approximately to Nernst formula.

The reduction in acidic solution is, of course, due to the deposition of hydrogen ions, and in neutral solution due to the ionic splitting of water molecules.

In alkaline solution, however, is quite contrary to the value expected from Nernst formula, i. e. in 0.1 n NaOH deviation of +0.176 V, in 1 n NaOH+0.365 to positive, which is quite unexplicable from the inorganic electrolytic reduction.

Three possible explanations have been proposed and discussed.

(1) Pseudoacid reaction. (Hantzsch's Pseudosäure)

(2) Direct electronic reduction.

(3) The retardation of reduction in acid media and normal reduction potential in alkaline media.

An explanation of reduction by assuming temporary deposition of metallic ions, which had been hitherto taken as possible, has been disproved by showing that electropositive metal such as zinc and lead have no influence upon reduction potentials of nirobenzol.

The effect of neutral salt upon reduction potential has been proved to be the salting out action of neutral salt.

The following general formula has been given, exclusive of alkaline solutions.

$$\pi = -\frac{RT}{2F} \ln \frac{k'}{C_{RNO_2}^{\frac{1}{m}} [H^{\cdot}]^2}$$

where $\frac{1}{m}$ is adsorption exponent.

For the same hydrion concentrations

$$\pi = -k'' + \frac{RT}{2mF} \ln C_{RNO_2}$$

where $m=1.26$ in acidic, $m=1.31$ in neutral and $m=2.2$ in alkaline solutions, showing higher adsorption in alkaline solution.

Part II. The influence of the cathodic potential on the adsorption of nitrobenzol.

(*The electro-potential adsorption of nitrobenzol.*)

The polarization curves observed at the mercury dropping cathode show very often a distinct maximum at which, the current after having reached a certain intensity, begins to decrease with the increase of voltage, which is never the case in inorganic electrolysis.

To investigate this phenomenon more closely, a number of experiments were carried out.

To give a clearer idea of meaning of current-voltage curve, a comparison has been made between non polarizable electrode and mercury electrode.

Two kinds of saturation curves are observable, one due to a lack of hydrogen ions and the other due to that of nitrobenzol.

The maximum current is observable in the case of nitrobenzol saturation curve.

It has been found that nitrobenzol has an influence upon the absolute zero potential of mercury drops, which is always characterized by the minimum oscillations of galvanometer.

The high adsorbability of nitrobenzol to zinc is known and the same can be said to mercury.

Taking the view of Langmuir, we can assume that nitrobenzol is adsorbed to mercury, arranging oxygen atom to the mercury surface.

From this stand point it is not unnatural to assume that the adsorption of nitrobenzol is due to electrostatical attraction between oxygen atom of nitrobenzol and mercury, the latter, of course, is much influenced by the polarization potential applied to mercury drops.

In treating the effective concentration (C) of nitrobenzol, it is much reasonable to take the concentration at the adsorptive layer, that is

$$C=k'(E-E_0)-k''[H^\cdot]+C_0$$

where E is the applid e. m. f. E_0 the absolute zero potential in the presence of nitrobenzol, C_0 the bulk concentration, $[H^\cdot]$ the hydrion concentration.

From these view points the present auther deduced a mathematical formula

$$E=-\frac{RT}{2F}\ln\frac{kI}{[H^\cdot]^2(k'(E-E_0)-k''[H^\cdot]+C_0)}$$

where E the applied e. m. f. and I the corresponding current intensity.

It follows

$$I=\frac{[H^\cdot]^2(k'(E-E_0)-k''[H^\cdot]+C_0)}{k}e^{-\frac{2EF}{RT}}$$

For the maximum current intensity i. e. for $\frac{dI}{dE}=0$

we have $$E-E_0=\frac{RT}{2F}+\frac{k''[H^\cdot]}{k'}-\frac{C_0}{k'}$$

In alkaline solution, where we can neglect the term $\frac{k''[H^\cdot]}{k'}$, $(E-E_0)$ must theoretically always smaller than $\frac{RT}{2F}=0.0126\,V.$

Difference between potential of maximum current and absolute zero potential has been experimentally found to be 0.0115 V which is, in fine accord with the theoretical value.

For higher hydrion concentration $(E-E_0)$ will become larger which is also the case in experiments.

Further the influence of neutral salt, i. e. its salting out action, has been determined numerically, e. g. for 0.1n NaCl 6.7% and for 1 n NaCl 60 % of the bulk

concentration of nitrobenzol present.

The possibility of applying this method for the determination of nitrobenzol has been proposed. (the concentration of nitrobenzol so far as 10^{-3} gr. mol in litre gives saturation wave.)

Attention must be drawn to the new factor in the organic electrolytic reduction of technical process in pursuing the maximum current efficiency, that is, the electro-potential adsorption of organic substance to the electrode.

On the Enzymic Actions of Malt Diastase, purified fractionally by Ethyl Alcohol, upon the various Kinds of Starch and Soluble Starch.

By Fumiwo Hemmi and Mitsuji Ito.

I. Purification of Malt Diastase by Ethyl Alcohol with Different concentrations.

The kilned malt for beer brewing was extracted with 20 % alcohol (vol. %). To the filtrate, strong alcohol was added making it altogether 71.5 %, 77.3 %, and 82.8 % in volume successively. From these three fractions of malt diastase were precipitated. The first fraction, precipitated from 71.5 % alcoholic solution, was gathered on a filter paper. Then the alcoholic content of the filtrate was increased to 77.3 % by a further addition of strong alcohol. From the filtrate separated from the second precipitate, the third fraction of enzyme was precipitated by 82.8% alcoholic solution. The three fractions of the enzyme thus obtained were well washed first with alcoholic solution of such concentration as precipitated the enzyme, then with absolute alcohol and ether several times, and afterward dried. Each fraction was dissolved in a definite quantity of water in regulating the concentration of enzyme.

II. Preparation and Purification of various Kinds of Starch and Soluble Starch.

Starch used in the present investigation was made and purified from the following eleven kinds of plant:

1. Erythrinum denscanis L.
2. Manihot aipi Pohl. (glutinous).
3. Maranta arundinacea L.

4. Oryza sativa L. (common).
5. Oryza sativa L. (common, up land).
6. Oryza sativa L. (glutinous).
7. Panicum frumentaceum Roxb.
8. Panicum miliaceum L. (glutinous).
9. Setaria italica Kth. var. germanica Trin. (glutinous).
10. Solanum tuberosum L.
11. Zea mays L.

Soluble starch was made from pure starch above prepared. Fifty grams of pure starch were put in a flask, containing 200 c.c. of dilute hydrochloric acid (1 vol. of 35.39% hydrochloric acid: 9 vols. of water) and kept at room temperature, well shaken twice a day. Fifteen days after, the upper solution was removed dy decantation. The soluble starch thus obtained was well washed with water for a long time, until no acid reaction was observed; then with alcohol and ether, and afterward dried. The starch paste and the soluble starch solution thus obtained were all neutral in reaction.

III. Experiments for Enzymic Actions of Malt Diastase.

The experiments for the liquefying and the sacchrifying powers of malt diastase were made separately, using different fractions of malt diastase, and various kinds of starch and soluble starch. 2 % and 4 % starch pastes, and 2 % and 5 % soluble starch solutions were used. The experiments were made at four stages of 2.5 or 4.5, 20 or 25, 45 or 50 and 100 hours respectively. Incubation, at 38°C. Toluene was added for antiseptic purpose as well as to prevent the evaporation of water during the incubation. The relative power of liquefaction of starch paste by malt diastase was determined by using Ostwald's viscosimeter and by color reaction with potassium iodide iodine solution. The relative power of saccharification of starch paste and soluble starch solution was measured by the Bertrand's method and estimated by volumes in c.c. of $KMnO_4$ solution used for titration.

IV. Results.

1. When the malt diastase was purified fractionally by ethyl alcohol with different concentrations, enzymic powers of each fraction of malt diastase were different. The relative powers of liquefaction and saccharification of the first and the second frations of the enzyme were both strong, especially the former was the strongest of three. The third fraction of malt diastase had weak powers of these

two enzymic actions and specially for potato starch and its soluble starch.

2. Both actions of lipuefaction and sacchrification of malt diastase upon various kinds of starch and soluble starch were different, according to the special properties of starch and soluble starch and to fractions of enzyme and also to their concentration.

3. The relative power of saccharification of malt diastase upon various kinds of starch was lower than that upon soluble starch, in every fraction of three, with the exception of potato starch and its soluble starch. Further investigations on the enzymic action of malt diastase upon potato starch and its soluble starch will be reported in a subsequent paper.

Feb. 28 th., 1925.

Feeding Experiments on the Nutrition of Chickens and Fowls.

By Masumi Kanai and Masanobu Matsuda.

The influences of vitamins and some kinds of proteins on the nutrition of chickens and fowls, and on their egg-production have been investigated as follows;-

1. Vitamins A and B are absolutely necessary for the growth of chickens. In case the diet lacks of them the growth stops and death is followed. This influence is more remarkable on the younger ones, and the effect of vitamin B seemes to be more rapidly noticed than that of A.

2. When chickens are fed with an amount of vitamin A and B in more than the necessary quantity, their bodily resistance becomes much greater as the additional amount is increased. Vitamin A is exceedingly more effective on chickens in this respect.

3. Vitamin C is also necessary for their growth, but its influence is not so great as that of A and B. The supply of this vitamin can be discontinued, after its necessary quantity is given, without any interference in the growth.

4, The effects of vitamins A and B on fowls are similar to those effects on chickens. When these vitamins are not supplied, the fowls cease to grow further, and their body-weights decrease. But fowls show a greater resisting power to the deficiency of A and B than do chickens. Vitamin B is more effective on fowls

than vitamin A, and shows identical influences with those on chickens.

5. Vitamin C is not necessary for the growth of fowls. With regard to egg-production the authors have to make another investigation.

6. The addition of vitamins A and B to the usual ration increase the egg-production. This influence is more pronounced in the case of A than of B.

7. As to the protein supply for the growth of chickens, pure proteins alone are not sufficient; but a certain quantity of soluble proteins must be added.

8. Fresh vegetable proteins have almost the same nutritive value as horse-fresh proteins for the growth of fowls, and when fresh proteins are given as a part of the indispensable food ration, the only other necessary proteins are those of fresh vegetables. (Chickens partly want some soluble proteins). Under these conditions they grow without showing any defect and increase greatly in their body weights.

Concernig the difference between the influences of fresh vegetable proteins and fresh proteins on the growth of fowls, the authors will discuss in another paper.

On the Occurrence of a Sulphur-containing Amino acid in Yeast.

By Satoru Odake.

Last year, Dr. U. Suzuki, T. Mori and the author isolated a new sulphur compound from the alcoholic extract of yeast, and gave the emperical formula (C_{11} H_{15} NSO_3 to it. Boiled with diluted acids, it was hydrolysed easily to adenin ($C_5H_5N_5$) and a new thiosugar ($C_6H_{12}SO_4$); so the authors concluded this componnd should be Adenyl-thiomethyl-pentose (U. Suzuki, S. Odake and T. mori;- The Journ. of the Agricul. Chem. Society of Japan, Vol. I, No. 2, p. 127-136, 1924, Biochemische Zeitschrift, B. 154, Heft, 3/6 S. 278-289, 1924.)

On studying further the alcoholic extract of yeast, the author isolated a sulphur containing amino acid in the following way:—

The alcoholic extract of yeast was evaporated in diminished pressure to a syrupy consistence and dissolved in a little water. A concentrated tannin solution was then added and the precipitate thus formed, was collected, decomposed with baryta water and filtered. The filtrate, freed from an excess of baryta, was evaporated to

a small volume, when the crystals of adenyl thio methyl pentose separated out and which were filtered off. To this filtrate, strong alcohol was added enongh to make the alcoholic content of the mixture 80% by volume. The voluminous precipitate thus formed, was filtered by suction, and recystallized several times from diluted alcohol. The crystals were found to be the mixture of leucin and a sulphur compound, but it was impossible to separate them by fractional cryrtallization. It was therefore dissolved again in water, and the saturated solution of mercuric chloride was added. The sulphur compound alone, forming an insoluble double salt with it, was precipitated and then decomposed with hydrogen sulphide. This treatment was repeated again and the resulted crystals were recrystallized from diluted alcohol. The yield of the purified compound was 0.6 gr. from about 20 tons of fresh yeast.

The sulphur compound thus obtained having the emperical formula $C_5H_{11}SNO_2$ is apparently a sulphur containing amino acid, as the analytical results of the free compound as well as of its derivatives show.

The purified compound is colourless and crystallizes in thin monoclinic plates. Heated in a capillary, it melts at 272–273°C (uncorr.) with decomposition. It is easily soluble in water, and in diluted alcohol, but insoluble in ether, benzene, etc. Its specific rotatory power is $[\alpha]_D^{16} = -11.77°$ in water. The aqueous solution of this compound gives a violet colour reaction with ninhydrin when warmed, but Millon's, diazo–, biuret–, and ferric chloride reactions are all absent. With $HgCl_2$ and $HgSO_4$, it gives a white precipitate, but it is precipitated neither by phosphotungstic acid nor by picric acid. Even a boiling strong alkali does not split sulphur from this compound in a form, detectable by sodium nitroprusside or by lead acetate, while both these reactions are positive, when it is fused with metallic sodium. In contrary to ethyl cystein this sulphur compound is quite stable against a boiling strong alkali, giving neither ammonia nor ethyl mercaptane. (Compare ; Brenzinger:– Zeitschrift. f. physiol chem. XVI. 563, 1892. Neuberg U. Mayer :– Zeitschr. f. physiol. chem. 44. 489, 1905). The copper salt $Cu(C_5H_{10}SNO_2)_2$ forms light blue thin monoclinic plates which are somewhat soluble in boiling water but insoluble in the cold. Its derivative of α–naphtyl isocyanate $C_{10}H_7NHCO–NHCH(C_5H_7S)COOH$ crystallizes in white long needles, melting at 178°C (uncorr). It is almost insoluble in water, ether etc., but dissolves easily in alcohol.

Recently, J. H. Müller isolated a new sulphur compound $C_5H_{11}SNO_2$ from hydrolytic products of casein and eggalbumin with sulphuric acid or caustic soda.

(J. H. Müller:– Journ. of Bact. VII. 300–325, 1922. Journ. of Biolog. chem. LVI. No 1. 1923.) The sulphur compound, isolated by the author from yeast, has entirely the same properties with it, except a little difference in the rotatory power. Although the constitution and the distribution of this compound are now in the course of investigation, it is clear that it must have been produced by autolysis of of yeast protein.

The author desires to express his sincere thanks to prof. Dr. U. Suzuki, for kind advice and giving the opportunity of publishing this paper.

Sinomenine and Dehydrosinomenine.
Part IV.

By Kakuji Goto.

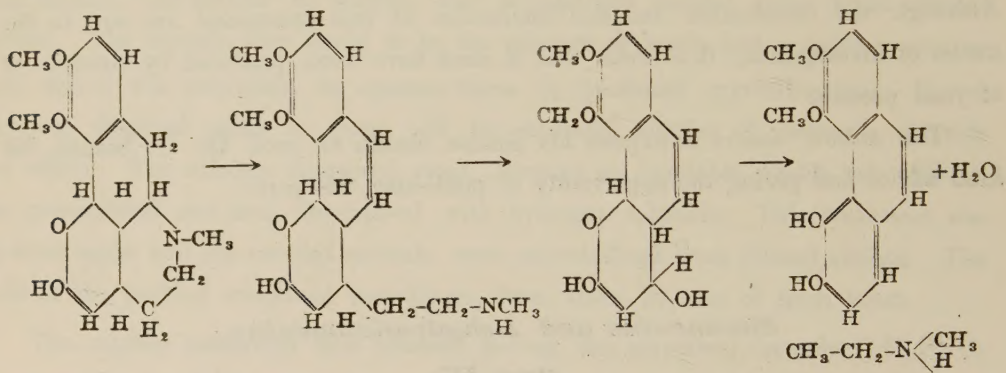
In the last report (this Journal, this vol., p. 50), it could not be decided whether the amine, obtained from sinomenine by the fusion with kali was methylvinylamine or methylethylamine. For, the melting point of the gold salt coincided with that of the methyethylaminechloroaurate, but the chloroplatinate melted seventeen degrees higher than that of the methylethylamine, while the analysis of the both salts could scarecely show any difference in these two amines.

The decision could be given, if sinomenineiodomethylate was fused with kali. For, in this case, the amine to be liberated must naturally be tertiary and the ethanolamine, if it was produced at all, could not loose water intermolecularly.

In this supposition sinomenineiodomethylate was boiled with 66 per cent caustic kali in the same way as with sinomenine, and the sinomenol was obtained in 40 per cent yield of the theoretical. But the amine, isolated in this case was undoubtedly dimethylethylamine (m. p. of the chloroaurate 222° with decomposition, Au=47.87 per cent; calc. as $C_3H_{11}NAuCl_4H$, Au = 47.81 percent and m.p. of the chloroplatinate 239° with decomposition, Pt=35.38 per cent; calc. as $(C_3H_{11}N)_2PtCl_6H_2$ Pt=35.22 per cent.). From this fact, it may be inferred that the amine obtained in the kali fusion of sinominine must have been methylethylamine and not methylvinylamine. The fact that the m. p. of its chloroplatinate seventeen degrees higher than that given in the literature was perhaps one of examples often met with auri–

and platini-chlorides of the lower fatty amines

The decomposition of sinomenine in the fusion with kali can, therefore, be expressed in the following scheme.



If so, sinomenol must be dioxydimethoxyphenanthrene ($C_{16}H_{14}O_4$) itself, and not its dihydride, as was supposed in the previous report. The comparison of the analytical data with the theoretical shows also clearly this fact. The molecular formulae of sinomenol and its derivatives, given in the same report, must, accordingly, be corrected as follows.

		Found		Calculated		Calculated on the basis sinomenol $C_{16}H_{16}O_4$	
		C	H	C	H	C	H
Sinomenol	$C_{16}H_{14}O_4$	70.71	5.83	71.08	5.22	70.58	5.89
Diacetyl-sinomenol.	$C_{20}H_{18}O_6$	1. 67.45 2. 67.88 3. 67.32	5.54 6.24 6.00	67.79	5.12	67.41	5.62
Dibenzoyl-sinomenol.	$C_{30}H_{22}O_6$	1. 75.59 2. 75.39	5.39 5.15	75.28	4.62	75.00	5.00
Dibenzoyl-sinomenol-chinone.	$C_{30}H_{20}O_8$	69.42	4.07	70.86	3.96	—	—
Dimethyl-sinomenol,	$C_{18}H_{18}O_4$	A. 72.59 B. 72.01	6.51 6.39	72.45	6.08	72.00	6.71

Sinomenine was methylated by diazomethane in status nascendi. Methylsinomenine, thus obtained, melts at 169° and contains three methoxyl groups (26.51 per cent; calc. as three methoxyl groups in $C_{20}H_{25}NO_4$, 27.11 per cent). Its hydrochloride melts at 265° and is very sparingly soluble in water. Methylsinomenine gives neither diazoreaction nor ferric chloride and potassium ferricyanide reactions. It gives a semicarbazone (m. p. 149–151°, N=14.54 per cent; calc. as $C_{21}H_{26}O_5N_5$ N=13,69 per cent.) so that the existence of the carbonyl and hydroxyl groups independently each other, could be shown on sinemenine itself.

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